



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 222/04, 228/02	A1	(11) International Publication Number: WO 96/20962 (43) International Publication Date: 11 July 1996 (11.07.96)
(21) International Application Number: PCT/US96/00007 (22) International Filing Date: 4 January 1996 (04.01.96) (30) Priority Data: 08/369,825 6 January 1995 (06.01.95) US (71) Applicant: HENKEL CORPORATION [US/US]; Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US). (72) Inventors: ARORA, Kartar, S.; 106 Harrison Forge Court, Chalfont, PA 18914 (US). JOHNSON, Grannis, S.; 286 Aquetong Road, New Hope, PA 18938 (US). THOMPSON, John, A.; 231 South 79th Street, Milwaukee, WI 53214 (US). (74) Agent: ORTIZ, Daniel, S.; Henkel Corporation, Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US).		(81) Designated States: JP, TR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: COPOLYMER OF VINYL SULFONIC ACID AND METHOD FOR TREATING LEATHER (57) Abstract The invention is a copolymer comprising 1 to about 20 percent by weight of vinyl sulfonic acid residues, 5 to 20 percent by weight of nonpolar or hydrophobic residues and 60 to 94 percent by weight of hydrophilic residues and a process for treating leather using the copolymer as a retanning agent.		

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COPOLYMER OF VINYL SULFONIC ACID AND METHOD FOR TREATING LEATHER

FIELD OF THE INVENTION

The invention is a copolymer of vinyl sulfonic acid and a method of use of the copolymer for treating leather.

BACKGROUND OF THE INVENTION

5 Copolymers containing vinyl sulfonic acid residues are known. They have been used in applications such as water desalinization and metal passivation, adhesives, coating materials and leather treating compositions. The copolymers contain vinyl sulfonic acid residues or salts thereof, residues of other hydrophilic or polar monomers and residues of nonpolar or hydrophobic monomers. The
10 composition of the copolymers is dependent on the end use for the copolymer.

RELATED ART

U.S. Patent 2,300,920 discloses self-emulsifying copolymers containing not more than 10% by weight of vinyl sulfonic acid or vinyl sulfonic acid salt residues, based on the weight of the other monomers in the copolymer. The
15 patent exemplifies an ethyl acrylate - sodium vinyl sulfonate copolymer containing 0.5 percent by weight of sodium vinyl sulfonate residues and a vinyl

acetate - sodium vinyl sulfonate copolymer containing 0.5 percent by weight of sodium vinyl sulfonate residues.

U.S. Patent 3,203,938 discloses a process for copolymerizing alkali metal vinyl sulfonate by use of a lower alcohol polymerization medium. Examples of copolymers of sodium vinyl sulfonate with acrylamide, with acrylic acid and with methacrylamide are disclosed. The patent discloses that the copolymers can be employed as tanning agents, emulsifying agents, flameproofing agents for fibrous materials, ion exchange resins, catalysts, water thickeners, cosmetics, in adhesives, in oil well drilling muds and as antistatic agents for synthetic hydrophobic textile materials.

U.S. Patent 3,657,201 discloses alternating copolymers containing residues of salts of sulfonic acid group containing moieties. The copolymers contain about 50 mole percent of the sulfonic acid group containing residues. The copolymers are disclosed as useful for forming films, fibers or moldings, as ion exchange resins and readily dyeable polymers.

U.S. Patent 3,682,224 discloses a method for preventing scale formation in a saline water evaporation process by including 1-10 ppm of a methacrylic acid - vinyl sulfonate copolymer with a ratio of methacrylic acid : vinyl sulfonate of from 50:50 to 25:75.

U.S. Patent 4,719,082 discloses use of vinyl sulfonic acid - methacrylic acid polymers as passivators for high pressure boilers. The polymers contain from 5-20 mole percent of vinyl sulfonate residues and 80 to 95 mole percent of methacrylic acid residues. The copolymer has a molecular weight of from 10,000 to 75,000 and preferably 20,000 to 50,000.

U.S. Patent 5,084,535 discloses a method for preparation of (meth)acrylic acid - vinyl sulfonic acid polymers by polymerizing the monomers by free radical initiation in a bed of particulate material. The copolymers contain from 100-70 percent by weight of (meth)acrylic acid residues and 0-30 percent by weight of vinyl sulfonic acid or vinyl sulfonic acid salt residue. The copolymers are useful grinding aids or dispersants for slurries of paper coating pigments and encrustation inhibitors for detergent applications. A copolymer of 5.6 percent by weight of sodium vinyl sulfonate residues and 94.4 percent by weight of acrylic

acid residues is exemplified.

KÔGYÔ KAGAKU ZASSHI Vol. 60, 1056-8 (1957) (CA Vol. 53 10837a 1959) discloses a study of the viscosity and gelation of acrylic acid-ethylene sulfonic acid copolymers in aqueous solution.

5 German Patent publication 1,469,837 (CA Vol. 83 60501n 1975) April 18, 1974, discloses use of a copolymer with a 30:10:60:1 ratio of acrylic acid : butyl acrylate : ethyl acrylate : vinyl sulfonic acid to stabilize an acrylic acid - ethyl acrylate - methyl methacrylate copolymer in an aqueous dispersion.

10 French Patent publication 1,383,924 January 1, 1965 (CA Vol. 63 13444f), discloses an acrylamide : acrylic acid : vinyl sulfonic acid copolymer in a weight ratio of 525:140:35.

German Patent publication 1,963,398, June 21, 1971 (CA Vol. 75 99003m) discloses a coating for polymer films formed from a copolymer of acrylic acid, butyl acrylate, vinyl sulfonate and styrene.

15 German Patent publication 1,965,588 December 30, 1969 (CA Vol. 75 118994d) discloses a 47:2:1 tert-butylacrylate: acrylic acid : vinyl sulfonic acid copolymer useful for forming foamed polymers with small cells.

German Patent publication 2,160,381 published June 14, 1973 (CA Vol. 79 79483x) discloses an acrylic acid - butyl acrylate - sodium ethene sulfonate - vinyl propionate copolymer produced by a continuous process.

20 French Patent publication 1,533,483 discloses a process for treating leather by impregnating the leather with a polymer formed from 5 to 100 percent by weight of vinyl sulfonic acid and 0 to 95 percent by weight of acrylic acid, acrylic acid esters, methacrylic acid and methacrylic acid esters. The patent exemplifies polymers formed from 100 percent sodium vinyl sulfonate, and copolymers of various ratios of from 10 to 90 percent by weight of acrylic or methacrylic acid with vinyl sulfonic acid.

25 British Patent specification 530,643 discloses a process for tanning leather using acrylic acid or methacrylic acid copolymerized with hydrophobic monomers.

30 U.S. Patent 2,220,867 discloses treating leather with a copolymer of acrylic or methacrylic acid with acrylates and other hydrophobic monomers.

U.S. Patent 3,945,792 exemplifies impregnating leather with a polymer formed from methacrylic acid and ethyl acrylate or a polymer formed from acrylic acid and butylacrylate.

5 U.S. Patent 4,526,581 discloses polymers for tanning leather formed from methacrylic acid and methyl, ethyl or butylacrylate containing at least 60 mole percent of methacrylic acid residues and more than 5 percent of C₁ to C₄ alkyl acrylate residues.

10 U.S. Patent 4,314,802 discloses a process for tanning leather by treating the leather with an aqueous dispersion or solution of a polymer formed from acrylic or methacrylic acid and optionally alkyl esters of acrylic, methacrylic acid, or sulfonated unsaturated drying oils followed by a treatment with a zirconium tanning composition having a 0-45 percent basicity by the Scharlemmer scale.

15 U.S. 4,631,063 discloses a process for treating mineral tanned leather by treating the leather with a water soluble polymer containing ethylenically unsaturated acrylic sulfonic acid, esters thereof and an ethylenically unsaturated aromatic sulfonic acid and salts thereof. Examples of the ethylenically unsaturated acrylic sulfonic acid are 2-acrylamide-2-methyl propane sulfonic acid, N(3-sulfopropyl-N-(meth)acrylamidopropyl-n,N-dimethyl ammonium betaine, sulfopropyl(meth)acrylic acid ester, styryl-sulfonic acid and alkali metal and
20 ammonium salts thereof. The polymers exemplified contain the sulfonic acid, acrylamide and acrylic or methacrylic acid residues. The sulfonic acid residue is present on the polymer in at least 3 mole percent and preferably at least 5 mole percent. The exemplification discloses polymers containing from about 5 to about 10 mole percent and about 10 to about 25 percent by weight of the
25 sulfonate, acrylamide and acrylic acid residues.

The prior art discloses that a large number of copolymers containing vinyl sulfonic acid residues with (meth)acrylic acid or (meth)acrylic acid ester residues are known and that many of the copolymers have been used to treat leather.

BRIEF SUMMARY OF THE INVENTION

30 According to the present invention a copolymer for treating leather is provided which comprises:

- 5
- a) 1.0 to about 20 percent by weight of vinyl sulfonic acid residues;
 - b) 5 to 20 percent by weight of nonpolar or hydrophobic monomer residues; and
 - c) 60 to about 94 percent by weight of hydrophilic ethylenically unsaturated carboxylic acid residues, the copolymers having a weight average molecular weight of from about 1,500 to about 15,000.

Preferably the copolymer comprises:

- 10
- a) 1.5 to about 10 percent by weight of vinyl sulfonic acid residues;
 - b) 5 to about 20 percent by weight of residues of at least one composition selected from the group consisting of amides of (meth)acrylic acid with C_4 to C_{10} amines, esters of (meth)acrylic acid with C_2 to C_8 alcohols, amides of α - C_2 to C_4 alkyl acrylic acid with C_4 to C_{10} amines and esters of α - C_2 to C_4 alkyl acrylic acid with C_2 to C_8 alcohols; and
 - c) about 70 to about 93.5 percent by weight of residues of at least one acid selected from the group consisting of (meth)acrylic acid, maleic anhydride or its equivalent maleic acid, itaconic acid, fumaric acid and α - C_2 to C_4 alkyl acrylic acid wherein the weight average molecular weight is from about 2,500 to about 10,000.
- 15
- 20

More preferably the copolymer comprises:

- a) 1.5 to 8 percent by weight of vinyl sulfonic acid residues;
 - b) 5 to about 20 percent by weight of residues of at least one ester of (meth)acrylic acid with at least one C_3 to C_8 aliphatic alcohol; and
 - c) about 72 to about 93.5 percent by weight of residues of (meth)acrylic acid, wherein the weight average molecular weight is from about 2,500 to about 10,000.
- 25

Most preferably the copolymer comprises:

- a) 1.5 to 6 percent by weight of vinyl sulfonic acid residues;
 - b) 5 to 20 percent by weight of at least one ester of acrylic acid with a C_3 to C_8 aliphatic alcohol; and
 - c) about 74 to about 93.5 percent by weight of methacrylic acid
- 30

residues wherein the copolymer has a weight average molecular weight of from about 3,000 to about 9,000.

The invention further comprises treating leather with the copolymer of the invention. The process comprises impregnating leather with the composition of the invention. The composition of the invention is particularly useful for retanning leather which has been tanned with an organic or mineral salt tanning agent. The composition of the invention can be applied to leather simultaneously with an organic or mineral salt tanning agent in the retanning process. Preferably the tanned leather is contacted with the composition of the invention then with an organic or mineral tanning agent and preferably a mineral tanning agent.

The retanned leather is light in color, stable to light and has improved softness and fill, a very fine grain and tight break.

DETAILED DESCRIPTION OF THE INVENTION

The copolymers of the invention comprise small amounts of vinyl sulfonic acid residues ($\text{CH}_2=\text{CH}-\text{SO}_3\text{H}$) or salts thereof. The vinyl sulfonic acid residues are present in the copolymer at from about 1.0 to about 20 percent by weight of the copolymer, preferably from 1.5 to about 10 percent by weight, more preferably from 1.5 to about 8 percent by weight of the copolymer, still more preferably from about 1.5 to less than 6 and more preferably less than 5 percent by weight of the copolymer and most preferably from about 2 to about 4 percent by weight of the copolymer. The small amount of the vinyl sulfonic acid residues in the copolymer provide for application of the copolymer at a lower pH than the pH at which a copolymer having only carboxylic acid groups can be used to impregnate leather. The lower pH at which the copolymers can be used is advantageous as the pH of leather tanned with mineral or organic tanning agents is in the acidic range.

The copolymer of the present invention contains small amounts, in the range of 5 to about 20 percent, preferably 5 to 15 percent, and most preferably 8 to 14 percent by weight of nonpolar or hydrophobic monomer residues. The nonpolar or hydrophobic monomer residues can be amides of (meth)acrylic acid with C_4 to C_{10} amines, esters of (meth)acrylic acid with C_2 to C_8 alcohols, amides

of α -C₂ to C₄ alkyl acrylic acid with C₄ to C₁₀ amines, esters of α -C₂ to C₄ alkyl acrylic acid with C₂ to C₈ alcohols. Preferably the amides contain from 4 to 8 carbon atoms in the amide group and the esters are esters of aliphatic alcohols having from 3 to 5 carbon atoms. The hydrophobic residues are preferably
5 residues of amides or esters of (meth)acrylic acid and more preferably esters of acrylic acid. When the nonpolar or hydrophobic moieties comprise esters or amides of methacrylic acid, the leather impregnated with the composition of the invention tends to be harder and stiffer than when impregnated with an amide or ester of acrylic acid. The long chain length amide and ester residues impart
10 additional softness to the treated leather. Methacrylic acid nonpolar or hydrophobic residues provide a stiffer and harder leather. As used herein, (meth)acrylic refers to acrylic acid, methacrylic acid or mixtures thereof.

The composition of the present invention can include hydrophobic moieties which are the residues of ethylenically unsaturated essentially
15 hydrocarbon moieties containing from about 4 to about 10 carbon atoms. Hydrocarbons such as butene, amylene, hexene, heptene, octene, styrene, α -methyl styrene, pentene, dipentene, vinyl naphthalene, and the like can be useful to provide the hydrophobic residues in the copolymer of the invention. Essentially hydrocarbon residues tend to provide treated leather which is harder
20 and stiffer than leather which has been impregnated with a copolymer which does not contain essentially hydrocarbon moiety residues.

The copolymer of the invention contains hydrophilic moieties which are the residues of ethylenically unsaturated carboxylic acids or their anhydrides. Ethylenically unsaturated carboxylic acid such as (meth)acrylic acid, maleic
25 anhydride or its equivalent maleic acid, α -C₂ to C₄ alkyl acrylic acid, fumaric acid, itaconic acid and the like can be useful in the copolymers of the invention.

Preferred hydrophilic moieties are the residues of acrylic acid, maleic acid, and methacrylic acid. The hydrophilic carboxylic acid residues are present at from about 60 to about 94 percent by weight of the copolymer, preferably from
30 about 70 to about 94 percent by weight of the copolymer and most preferably from about 74 to about 93.5 percent by weight of the copolymer. The hydrophilic moieties enhance the solubility of the copolymer in water to provide for ease of

penetration of the leather. The copolymer is generally partially neutralized to provide a copolymer which is soluble in water. The presence of the vinyl sulfonic acid residues enables the copolymer to become soluble at a lower pH which aids in retanning leather.

5 The aqueous solution of the copolymer of the present invention can rapidly penetrate the leather and provide a lighter colored, softer and fuller leather than obtained by use of prior art polymers. The copolymer of the invention can also be used as a tanning or pretanning composition.

10 The copolymers of the invention have a weight average molecular weight of from about 1,500 to about 15,000 and preferably from about 2,500 to about 10,000 and most preferably from 3,000 to about 9,000. The low molecular weight and water solubility of the polymer provides a copolymer which is readily soluble in water and can easily penetrate leather. The combination of properties of the copolymer provides a material which is useful for treating leather and
15 particularly for retanning leather.

 The copolymers of the present invention are prepared by free radical polymerization. The copolymers can be prepared in bulk, in a solvent or in water. It is preferred to prepare the copolymer in a solvent or a mixture of a solvent and water. The preferred solvents are lower alcohols such as methyl, ethyl, propyl,
20 isopropyl, butyl and isobutyl alcohols. The low boiling point solvents are particularly useful since the solvent is removed after the polymerization and the copolymer prepared as a solution or dispersion in water. During the polymerization a small amount of an alkaline material such as sodium hydroxide or ammonia is introduced into the polymerization zone. At the end of the
25 polymerization, the solvent is removed and some additional alkaline material added to solubilize or disperse the copolymer in water. The concentration is adjusted to the range at which the copolymer is sold or to which it is diluted for use. Generally a 15 to about 60 percent by weight solution or dispersion of the copolymer is prepared. The solution is diluted to a 1 to about 30 percent (active)
30 solution or dispersion in water for use in impregnating leather.

 The copolymer can be prepared by heating a 1:1 by weight mixture of deionized water and isopropanol under nitrogen to a temperature of about 80°

C. A solution of a water soluble free radical initiator such as sodium persulfate is prepared. A mixture of the monomers to be polymerized, ammonia and water is prepared. The solution of the initiator and the mixture of the monomers, water and ammonia are concurrently introduced into the water alcohol mixture maintained at a temperature of 80° C over a period of several hours. After the addition of the monomers has been completed the polymerization mixture is maintained at 80° C for about an hour. The temperature is then slowly raised to about 100° C and an alcohol water mixture is distilled from the polymer. When the temperature reaches 100° C, the distillation is stopped and water and additional ammonia are added to the mixture until the mixture becomes clear and the desired copolymer concentration has been obtained. The concentration of the copolymer solution or dispersion is generally in the range of about 30 to about 60 percent by weight. The volatile organic solvent is reduced in the composition to less than about 5 percent and most preferably to less than about 3 percent by weight of the mixture. Vacuum distillation can also be used to remove volatile organic compounds from the dispersion and/or solution of the copolymer.

The copolymers are useful for treating leather and particularly for retanning leather. As is well known in the art, raw leather must be tanned and treated to become a useful material. Untanned leather is subject to attack by microorganisms and does not have pleasing aesthetic properties. The tanning and finishing of leather produces a tanned and treated leather which is resistant to attack by microorganisms, is generally stronger, more flexible and softer than untanned and untreated leather.

A tanning process utilizing a polymer or copolymer of (meth)acrylic acid as a tanning agent and a retanning procedure with an aluminum or a zirconium tanning salt or mixture thereof is fully disclosed in U.S. 4,334,876. In a conventional tanning process the pickled and bated leather is first contacted with mineral or vegetable tanning salts. Tanning mineral salts such as chromium⁺⁺⁺, aluminum salts and zirconium salts are the most common mineral tanning salts in use today.

The organic tanning agents comprise extracts of parts of certain plants

and particularly parts of certain trees and shrubs. The organic tanning agents are complex mixtures containing tannic acid or its salts and various polyphenol materials.

5 At present chromium*** tanning salts are the most commonly used tanning salts. However, due to environmental concerns, there is a constant search to find new materials or new methods which will produce leather with the same characteristics as "chrome tanned" leather without the detrimental effects to the environment.

10 The tanning process is a series of process steps in which rawhide is contacted with a series of aqueous mixtures generally in a rotating perforated drum. First the salt preservative is washed from the rawhide. In all the tanning and finishing steps, the pH of the aqueous phase is carefully adjusted to maintain the leather in an acidic condition. The pH is adjusted with materials such as formic or acetic acid or salts such as sodium acetate.

15 When the salt preservative has been washed from the leather, the pH of the leather is adjusted by tumbling the leather in an aqueous solution at the desired pH. The pH adjusted rawhide is then contacted with an aqueous solution of a tanning material which can be a chromium, aluminum or zirconium tanning salt or an organic tanning material. The rawhide is contacted with the solution
20 of the tanning salts for a sufficient length of time for the tanning salts to penetrate through the entire hide and to react with the substrate of the leather. The tanning procedure protects the leather from attack by microorganisms and improves the strength of the leather.

25 Tanned leather is usually subjected to wet-end procedures such as retanning, fat liquoring and coloring to improve the aesthetic properties of the material known as tanned leather.

30 In the wet-end process, the leather which has been tanned is generally retanned. In the retanning process, the tanned leather is contacted with aqueous mixtures of various agents to impart special properties to the leather. Leather properties such as strength, softness, flexibility, evenness of dyeing, fullness, water resistance and the like are generally adjusted by retanning and coloring.

In the present invention, preferably tanned leather is contacted with the

composition of the invention. The tanned leather is contacted with an aqueous solution or dispersion of the copolymer of the invention. The copolymer of the invention is added to the aqueous solution in an amount (active substance) to provide from about 1 to about 10 percent by weight of the copolymer of the leather being treated. The 1 to about 10 percent by weight of the copolymer of the leather is dissolved or dispersed in an amount of water of from 100 to about 300 percent of the weight of the leather. The leather is tumbled for a sufficient length of time to evenly impregnate the leather with the copolymer. The pH of the dispersion is adjusted to prevent too rapid absorption of the dispersion by the leather which can form a crust at the surface of the leather.

When the major portion of the copolymer has been absorbed by the leather, the pH of the aqueous bath can be lowered and the copolymer which remains in the dispersion is rapidly absorbed into the leather. The leather which has been treated with the copolymer of the invention can then be contacted with fat liquoring materials to further enhance the properties of the leather. In an alternate embodiment, the tanned leather can be contacted in a single step by an aqueous bath containing a solution or dispersion of the copolymer of the invention and the fat liquoring materials. The fat liquoring materials are oil and fat derived materials and can include sulfated saturated or unsaturated and hydroxyl containing fatty acids.

After the treatment with the copolymer of the invention, the treated leather can be treated with a mineral or organic tanning material. In an alternate embodiment, the mineral or organic tanning materials can be mixed with the solution and dispersion of the copolymer and the leather treated with the mixture in a single step.

The leather while still wet can be dyed in the same apparatus as the leather was retanned. In some processes the leather is dyed during one of the retanning steps by including the dye in admixture with the solution of the copolymer of the invention or the fat liquor materials.

The treated leather is washed free of soluble materials and dried. The dried treated leather can be further finished by application of various surface coating materials.

The general outline of a leather treating process presented above illustrates the major process steps. However, the process can be varied in many ways depending on the type of leather being treated, the experience of the operator and the properties of the leather product which are required.

5 The leather treating process is generally carried out at mild temperatures in the range of about 25° C to about 60° C at least before tanning since elevated temperatures can cause shrinking of the leather. The temperatures, amounts of solutions, the pH and concentrations of reagents used in leather treating processes are well known to one skilled in the leather treating art. The
10 parameters of the process depend on the source of the leather and the characteristics required in the finished leather. The leather processing art is complex and many schemes and processes for treating leather have been successfully developed. The present process is one step in the leather preparation process and provides useful properties to leather in conjunction with
15 other treatments.

 The leather, after impregnation with the copolymer of the invention, is generally treated to further modify its properties. The leather can be further tanned with mineral or vegetable tanning agents, the leather can be oiled to modify its feel, flexibility, softness, water resistance, color and scuff resistance.
20 All of these treatments are well known to one skilled in the art.

 The leather used in the following examples was full grain leather which had been chrome-tanned. The chrome-tanned leather was impregnated with the copolymer composition under the following conditions:

Procedure for Treatment of Leather with Amphiphilic Copolymers

	Process	Amount and Agent ¹	Temperature °C	Time Minutes
	Wash	300% Water 0.2% Formic Acid	40	15
	Drain	—	—	—
5	Rinse	300% Water	40	30
	Wash	150% Water	40	120
	Syntan	150% Water 5.5% Amph. Polymer ²	50	120
	Fixing	0.8% Formic Acid	—	30
	Drain	—	—	—
10	Chrome	150% Water 2% Tanolin R ³	50	30
	Chrome	2% Tanolin R ³	—	60
	Drain	—	—	—
	Wash	300% Water	40	10
	Drain	—	—	—
15	Wash	300% Water	40	10

1. Amounts refer to the weight of blue-stock.

2. Active substance.

3. Chrome-tanning material product of Rohm & Haas Co.

20 The treated leather was horsed overnight, dried on a vacuum drier to 12-14% moisture content and lightly staked prior to evaluation. The evaluation of chrome-tanned leather treated as above with various amphiphilic polymers is shown in Table 1.

Preparation of Copolymers

Deionized water was used for preparation of all copolymers. Aqueous size exclusion chromatography was used to determine molecular weight of copolymers using narrow molecular weight distribution poly(acrylic acid) standards. A suitable reaction apparatus for preparation of copolymers comprises a resin kettle of suitable size equipped with condenser, stirrer, heating mantle with means to measure and control temperature such as a Jack-o-matic™ with an on-off controller, fluid metering pumps and means for maintaining a nitrogen atmosphere.

Abbreviations used: AA = Acrylic acid, AMPS = 2-Acrylamidopropane sulfonic acid, BA = Butyl acrylate, BMA = n-Butyl methacrylate, EA = Ethyl acrylate, EHA = 2-Ethylhexyl acrylate, SVS = Sodium vinyl sulfonate, MAA = methacrylic acid.

Example 1

Copolymer of 85.6% MAA/11.7% BA/2.7% SVS. This copolymer was prepared from a monomer mixture of 326.7 g MAA, 44.4 g BA, 42.0 g SVS(25% by weight solution), 33.3 g ammonium hydroxide and 75 g water and an initiator solution of 45.8 g sodium persulfate and 85 g water. A mixture of 359.1 g isopropanol and 359.1 g water in a reaction kettle was heated to 80° C with stirring under a nitrogen atmosphere. A concurrent addition of monomer mixture and initiator solution was made to the reactor over 2 hours while maintaining the reaction temperature at 80 ± 2 C. The reaction mixture was held at this temperature for one hour after completion of the addition. Volatiles (430 g) were removed by heating the reaction mixture to 100° C and 229 g water and 27 g ammonium hydroxide were added to obtain a copolymer solution with 37.4% solids. The copolymer was found to have a weight-average molecular weight of 5,940 and number-average molecular weight of 1,760 by aqueous gel permeation chromatography (GPC) with respect to poly(acrylic acid) standards.

The leather was treated with the polymer according to the procedure set out above and evaluated for whiteness, grain texture (breach), UV light

resistance, hexane extractibles, softness, ease of lubrication, fullness and flexibility.

Example 2

Copolymer of 64.1% AA/14.5% AMPS/21.4% BA. This copolymer was prepared from a monomer mixture of 246.7 g AA, 82.2 g BA, 56.0 g AMPS, 53.4 g isopropanol and 122.3 g water and an initiator solution of 6.2 g sodium persulfate in 43.8 g water. A mixture of 330.3 g isopropanol and 90.3 g water was heated to 80° C under a nitrogen atmosphere in a reaction kettle. A concurrent addition of the monomer mixture and initiator solution was made over two hours while maintaining the reaction temperature at 80° C. A solution of 0.62 g of tert-butyl peroctoate in 4.4 g IPA was added after completion of polymerization. Water (475 g) was added and volatiles removed by heating the reaction mixture to 100° C and distillation to obtain a 37.4% by weight solution of the copolymer which had weight-average and number-average molecular weight of 5,510 and 1,810, respectively.

Example 3

Copolymer of 86.2% MAA/13.8% AMPS. The reactor was charged with 130 g isopropanol and 35 g deionized water. The solvent mixture was heated to 80° C under a nitrogen sparge. A mixture of 129 g MAA, 20.7 g AMPS and 45 g deionized water was prepared and a solution of 16.6g of sodium persulfate in 56 g deionized water was prepared. A concurrent addition of monomer mixture and initiator solution was made over two hours. After completion of the addition the reaction mixture was allowed to remain at 80° C for one hour. The product was transferred to a distillation flask with 250 g deionized water and isopropanol was removed by distillation to head temperature of 99.5° C. Additional water (250 g) was added to obtain 800 g of a copolymer dispersion of 22.7% solids.

Example 4

Polymer of MAA. The reactor was charged with 130 g isopropanol and 35 g deionized water. A mixture of 162 g MAA and 40 g deionized water was prepared. Sodium persulfate (20 g) was dissolved in 60 g deionized water.

5 The mixture of solvents was heated to 80° C under nitrogen sparge. A concurrent addition of monomer mixture and initiator solution was made over two hours. During the course of this addition more solvents (65 g isopropanol and 17.5 g deionized water) were added to reduce viscosity. The reaction mixture was maintained at 80° C for one hour after completion of the addition
10 of monomer and initiator and then transferred to a distillation flask with 500 g water. After distillation of isopropanol, 749 g of a solution of poly(methacrylic acid) with 24% solids was obtained.

Example 5

Copolymer of 89.2% MAA/10.8% AMPS. A reactor was charged with
15 130 g isopropanol and 35 g water. A monomer mixture of 146 g MAA, 17.6 g AMPS and 45 g water was prepared. A solution of 18.2 g sodium persulfate in 66 g water was prepared. The solvent mixture was heated to 80° C under nitrogen sparge. A concurrent addition of monomer mixture and initiator solution was made over two hours. After completion of addition the reaction
20 mixture was held at 80° C for 0.5 hours and then transferred to a distillation flask with 500 g water. After distillation of isopropanol 682 g of a solution of copolymer with 26.2% solids was obtained.

Example 6

Copolymer of 90.9% MAA/9.1% SVS. The reactor was charged with
25 139 g isopropanol and 38 g water. A monomer mixture was prepared from 129 g MAA, 52 g SVS (25% by weight solution) and sufficient water to obtain 420 ml. Initiator solution was prepared by dissolving 15 g sodium persulfate in sufficient water to obtain 50 ml solution. Solvent mixture in the reactor was heated to 80° C under a nitrogen sparge. Concurrent addition of monomer
30 mixture and initiator solution was made over two hours and the reaction

mixture was held at 80° C for another two hours. The product was transferred to a distillation flask and isopropanol was distilled off. Water (100 g) was added to obtain a solution of the copolymer with 33.2% solids. Molecular weight: weight average 6,410; number average 1,930.

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Example 7

Copolymer of 85% EA/15% MAA. This example was made according to Example 1 of US patent 3,103,447. A two-liter, four-neck, round-bottom flask equipped with a stirrer, a reflux condenser, heating mantle, temperature controller (Jack-o-matic®) and a metering pump was used. The flask was charged with 780 g water and heated to 95° C with stirring. Ammonium persulfate (7.0 g) was added to the flask at 95° C. Immediately thereafter, addition of a mixture of 187 g EA and 33 g MAA was started at a uniform rate with a metering pump. The addition of monomer mixture was completed in 24 min. The reaction was continued at 95° C for another 0.5 h and then the product was cooled to 61° C. Addition of 22.9 g ammonium hydroxide was made over 5 min. to obtain 1002 g of a clear solution of the copolymer, solids 21.3%, pH 8.1, viscosity 60 cpoise (Brookfield, RV#3 at 60 RPM).

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Example 8

Copolymer of 62% EA/28% BMA/10% MAA. This example was prepared similar to Example 8 above using a monomer mixture containing 136.4 g EA, 61.6 g BMA and 22.0 g MAA. The copolymer solution was neutralized with 15.8 g ammonium hydroxide had 21.5% solids, pH 8.4 and viscosity of less than 20 cpoise (Brookfield, RV#3 at 60 RPM).

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Example 9

Copolymer of 27.3% MAA/72.7% EHA. This example was performed according to the teaching of EP 0,498,634. The polymerization was conducted under nitrogen atmosphere in a one-liter, four-necked round bottom flask equipped with a stirrer, a reflux condenser, heating mantle and temperature controller (Jack-o-matic®). The flask was charged with 185 g water, 4 g

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sodium lauryl sulfate, 1 drop of sulfuric acid and 0.15 g of a 2 weight % solution of ferrous sulfate. The mixture was then heated to 60° C. The monomers (60 g MAA and 160 g EHA) were emulsified with 10.0 g n-dodecane thiol, 96 g water and 4 g of sodium lauryl sulfate. The emulsified monomer mixture was fed simultaneously with initiators (0.6 g ammonium persulfate diluted with 22 g water and 0.6 g sodium metabisulfite diluted with 22 g water) to the reaction flask over 2.5 h. The reaction mixture was held at 60° C for about two hours, and then 0.1 g of sodium metabisulfite and 0.1 g ammonium persulfate with 5 g of water were added. After another hour at 60° C, the batch was allowed to cool and neutralized with 9.0 g of 25% sodium hydroxide. The copolymer was found to have 40.8% solids and a viscosity of 70 cpoise (Brookfield, RV#3 at 60 RPM).

Example 10

Copolymer of 20% MAA/80% EHA. This copolymer of this example was prepared in a manner similar to that of Example 9 above. The reaction flask was charged with 370 g water, 8 g sodium lauryl sulfate, 0.3 g of a 2 weight % solution of ferrous sulfate and 2 drops of concentrated sulfuric acid. The monomers (80 g MAA and 320 g EHA) were emulsified with 20 g n-dodecanethiol, 192 g water and 8 g sodium lauryl sulfate. Contents of the reaction flask were heated to 60° C. The emulsified monomer mixture was fed simultaneously with initiators (1.2 g sodium metabisulfite dissolved in 44 g water and 1.2 g ammonium persulfate dissolved in 44 g water) to the reaction flask over 3.5 h. After about one hour 0.1 g sodium metabisulfite, 0.1 g ammonium persulfate and 5 g water were added. The heat was stopped after another seventy five minutes and the copolymer was neutralized with 12 g of 25% sodium hydroxide solution. The copolymer was found to have 37.8% solids, pH 5.2 and 40 cpoise viscosity (Brookfield, RV#3 at 60 RPM).

The properties of leather treated with amphiphilic copolymers as described above and commercial amphiphilic copolymers used for re-tanning of leather are shown in Table 1. Properties such as appearance, fullness (plumpness), firmness, flexibility (resilience), grain texture, ease of lubrication

and color (degree of whiteness) were subjective properties evaluated by person(s) skilled in the art.

Table 1.

5	Property ¹	Polymer			
		Example 1	Example 2	Example 3	Example 4
	Appearance	++	+	+	+
	Fullness (plumpness)	++	+	+	+
	Firmness	++	+	+	+
	Flexibility (resilience)	o	o	o	o
10	Grain Texture	++++	o	+	+
	Ease of Lubrication	o	o	o	o
	Color (degree of whiteness)	++++	++	++	++
	Hexane Extractables	+	o	o	+
15	Light Fastness	++	o	o	o
	Density, g/cm ³	0.636	0.676	0.677	0.605
	Tensile Strength ² , psi	2325	2121	1505	2370
	Elongation at break ² , %	26.4	41.7	39.5	37.1
	Tensile Modulus ² , psi	10450	5929	4493	7919
20	Tear Strength ³ , lb.	16.2	28.6	29.8	36.6
	Tear Strength ³ , lb/in	164	261	259	289

Table 1 (contd.)

Property ¹	Polymer Used			
	Example 5	Example 6	Example 7	Example 8
Appearance	+	+	-	-
Fullness (plumpness)	+	+	-	-
5 Firmness	+	+	-	-
Flexibility (resilience)	o	o	-	-
Grain Texture	+	o	-	-
Ease of Lubrication	o	o	-	-
10 Color (degree of whiteness)	++	++	-	-
Hexane Extractables	o	o	o	o
Light Fastness	o	o	-	-
Density, g/cm ³	0.566	0.660	0.624	0.647
Tensile Strength ² , psi	1909	1731	1989	1948
15 Elongation at break ² , %	40.2	35.5	50.1	68.7
Tensile Modulus ² , psi	5895	6023	7310	3569
Tear Strength ³ , lb.	29.6	30.3	26.6	26.7
Tear Strength ³ , lb/in	265	266	237	246

Table 1 (continued).

Property ¹	Polymer Used			
	Example 9	Example 10	Example 11 ⁴	Example 12 ⁵
Appearance	—	—	o	—
Fullness (plumpness)	-	-	o	—
5 Firmness	—	—	+	—
Flexibility (resilience)	-	-	+	-
Grain Texture	—	—	+	-
Ease of Lubrication	—	—	o	o
10 Color (degree of whiteness)	—	—	o	-
Hexane Extractables	o	o	o	o
Light Fastness	o	o	o	o
Density, g/cm ³	0.668	0.658	0.625	0.658
Tensile Strength ² , psi	2166	1984	1805	1721
15 Elongation at break ² , %	57.2	80.2	65.0	30.5
Tensile Modulus ² , psi	4666	3135	3785	7858
Tear Strength ³ , lb.	33.5	33.5	30.9	28.5
Tear Strength ³ , lb/in	308	320	242	253

Table 1 (continued).

Property ¹	Polymer Used		
	Example 13 ⁶	Example 14 ⁷	Example 15 ⁸
Appearance	—	—	—
Fullness (plumpness)	—	—	—
5 Firmness	—	—	—
Flexibility (resilience)	-	-	—
Grain Texture	-	—	—
Ease of Lubrication	o	-	—
10 Color (degree of whiteness)	-	-	—
Hexane Extractables ⁹	o	o	—
Light Fastness ¹¹	o	o	—
Density ¹⁰ , g/cm ³	0.575	0.648	0.672
Tensile Strength ² , psi	1676	2140	4883
15 Elongation at break ² , %	45.7	67.4	34.7
Tensile Modulus ² , psi	5308	3745	17170
Tear Strength ³ , lb.	40.2	41.6	35.3
Tear Strength ³ , lb/in	338	306	338

20 1. Key: "-" indicates one degree of decrease in performance, "o" indicates comparable performance, "+" indicates one degree of improvement in performance when compared to Blue Stock.

2. Measured with INSTRON® per ASTM D-2209-90.

3. Per ASTM D-1004-66.

4. LEUKOTAN 970 (Product of Rohm & Haas Co.).

25 5. LEUKOTAN 1027 (Product of Rohm & Haas Co.).

6. LEUKOTAN 1028 (Product of Rohm & Haas Co.).

7. ACRY SOL™ RM5 (Product of Rohm & Haas Co.).

8. Blue-stock

9. Measured per ASTM D-3495-83.

30 10. Measured per ASTM D-2346-68.

11. Measured after 72-96 hr. exposure to UV light.

Table 1 clearly shows the improvement in leather properties when leather is treated with the amphiphilic copolymer of the invention which contains vinyl sulfonic acid residues. Small amounts of residues of vinyl sulfonic acid or its salts incorporated into the polymer chain enhances grain texture, color, fullness and firmness of the leather when compared to leather which does not contain residues of vinyl sulfonic acid or its salts. The combination of the (meth)acrylic acid, nonpolar or hydrophobic monomer residues and vinyl sulfonic acid residues provides properties to leather not achieved by treatment with known compositions.

In addition, as shown in Table 1, leather treated with the composition of the invention, has an unexpectedly high Tensile Modulus when compared to leather treated with other polymers not containing vinyl sulfonic acid and nonpolar or hydrophobic residues. The high tensile modulus is an indicator of closer fiber packing which also aids in providing an improved grain texture to the leather.

The color and grain texture of leather treated with the polymers of the invention are outstanding. The appearance, fullness, firmness and light fastness of leather treated with the polymer of the invention are excellent. The combination of the properties imparted to leather including the high tensile modulus has not been achieved with leather treating and retanning materials known heretofore.

We Claim:

1. A copolymer comprising:
 - a) 1.0 to about 20 percent by weight of vinyl sulfonic acid residues;
 - b) 5 to about 20 percent by weight of nonpolar or hydrophobic monomer residues; and
 - c) 60 to about 94 percent by weight of hydrophilic ethylenically unsaturated carboxylic acid residues, the copolymer having a weight average molecular weight of from about 1,500 to about 15,000.
2. The copolymer of claim 1 comprising:
 - a) 1.5 to about 10 percent by weight of vinyl sulfonic acid residues;
 - b) 5 to about 20 percent by weight of residues of at least one composition selected from the group consisting of amides of (meth)acrylic acid with C₄ to C₁₀ amines, esters of (meth)acrylic acid with C₂ to C₄ alcohols, amides of an α -C₂ to C₄ acrylic acid with C₄ to C₁₀ amines, and esters of α -C₂ to C₄ acrylic acid with C₂ to C₆ alcohols;
 - c) about 70 to about 93.5 percent by weight of residues of at least one acid selected from the group consisting of (meth)acrylic acid, maleic anhydride, itaconic acid, fumaric acid and α -C₂ to C₄ alkyl acrylic acids.
3. The copolymer of claim 1 comprising:
 - a) 1.5 to 10 percent by weight of vinyl sulfonic acid residues;
 - b) 5 to about 20 percent by weight of residues of at least one ester of (meth)acrylic acid with a C₃ to C₆ aliphatic alcohol; and
 - c) 70 to about 93.5 percent by weight of (meth)acrylic acid.
4. The copolymer of claim 1 comprising:
 - a) 1.5 to about 6 percent by weight of vinyl sulfonic acid residues;

- b) 5 to about 20 percent by weight of at least one ester of acrylic acid with a C₃ to C₆ aliphatic alcohol; and
- c) about 74 to about 93.5 percent by weight of methacrylic acid residues wherein the copolymer has a weight average molecular weight of from about 3,000 to about 9,000.

5. A composition of claim 1 comprising:

- a) 1.5 to less than 5 percent by weight of vinyl sulfonic acid residues;
- b) 5 to 15 percent by weight of butyl acrylate residues; and
- c) 80 to 93.5 percent by weight of methacrylic acid residues.

6. A composition of claim 1 comprising:

- a) about 2 to about 4 percent by weight of vinyl sulfonic acid residues;
- b) about 8 to about 14 percent by weight of butyl acrylate residues; and
- c) about 82 to about 90 percent by weight of methacrylic acid residues.

7. A method for treating leather which comprises: impregnating the leather with an aqueous solution or dispersion of a polymer comprising:

- a) 1.0 to about 20 percent by weight of vinyl sulfonic acid residues;
- b) 5 to about 20 percent by weight of nonpolar or hydrophobic monomer residues; and
- c) 60 to about 94 percent by weight of hydrophilic ethylenically unsaturated carboxylic acid residues, the copolymer having a weight average molecular weight of from about 1,500 to about 15,000.

8. The method of claim 7 wherein the polymer comprises:

- a) 1.5 to about 9 percent by weight of vinyl sulfonic acid residues;

- 5 b) 5 to about 20 percent by weight of residues of at least one composition selected from the group consisting of amides of (meth)acrylic acid with C₄ to C₁₀ amines, esters of (meth)acrylic acid with C₂ to C₄ alcohols, amides of an α -C₂ to C₄ acrylic acid with C₄ to C₁₀ amines, and esters of α -C₂ to C₄ acrylic acid with C₂ to C₈ alcohols;
- 10 c) about 71 to about 93.5 percent by weight of residues of at least one acid selected from the group consisting of (meth)acrylic acid, maleic anhydride, itaconic acid, fumaric acid and α -C₂ to C₄ alkyl acrylic acids,
- the copolymer having a weight average molecular weight of from about 1,500 to about 15,000.

- 15 9. The method of claim 7 wherein the polymer comprises:
- a) 1.5 to 10 percent by weight of vinyl sulfonic acid residues;
- b) 5 to about 20 percent by weight of residues of at least one ester of (meth)acrylic acid with a C₃ to C₆ aliphatic alcohol; and
- c) 70 to about 93.5 percent by weight of (meth)acrylic acid,
- 20 wherein the copolymer has a weight average molecular weight of from about 1,500 to about 15,000.
10. The method of claim 9 wherein the weight average molecular weight of the copolymer is from about 3,000 to about 9,000.
- 25 11. The method of claim 7 wherein the polymer comprises:
- a) 1.5 to about 6 percent by weight of vinyl sulfonic acid residues;
- b) 5 to about 20 percent by weight of at least one ester of acrylic acid with a C₃ to C₆ aliphatic alcohol; and
- c) about 74 to about 93.5 percent by weight of methacrylic acid residues wherein the copolymer has a weight average molecular weight of from about 1,500 to about 15,000.

12. The method of claim 11 wherein the copolymer has a weight average molecular weight of from about 3,000 to about 9,000.
13. The method of claim 7 wherein the copolymer comprises:
- a) 1.5 to less than 5 percent by weight of vinyl sulfonic acid residues;
 - b) 5 to 15 percent by weight of butyl acrylate residues; and
 - c) 80 to 93.5 percent by weight of methacrylic acid residues.
14. The method of claim 13 wherein the copolymer has a weight average molecular weight of from about 3,000 to about 9,000.
15. The method of claim 7 wherein the copolymer comprises:
- a) about 2 to about 4 percent by weight of vinyl sulfonic acid residues;
 - b) about 8 to about 14 percent by weight of butyl acrylate residues; and
 - c) about 82 to about 90 percent by weight of methacrylic acid residues,
- wherein the copolymer has a weight average molecular weight of from about 1,500 to about 15,000.
16. The method of claim 15 wherein the copolymer has a weight average molecular weight of from about 3,000 to about 9,000.
17. The method of claim 7 wherein the leather is impregnated with an aqueous solution or dispersion containing from 1 to 10% by weight of the copolymer, the copolymer present in an amount of 1 to 30% by weight of the leather at a temperature of from about 30° C to about 60° C.

INTERNATIONAL SEARCH REPORT

Int. .ional application No.
PCT/US96/00007

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08F 222/04, 228/02

US CL :526/287, 271; 8/94.33

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/287, 271; 8/94.33

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,244,988 (HUGHES ET AL) 14 September 1993, columns 5-7.	1-17
Y	DE, A, 1,469,837 (BASF AG) 16 January 1969, translation pages 3-5.	1-17
Y	FR, A, 1,533,483 (BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT) 19 July 1968, translation pages 3-5 and examples.	1-17

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

26 MARCH 1996

Date of mailing of the international search report

04 APR 1996 (04.04.96)

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Form PCT/ISA/210 (second sheet)(July 1992)*